METHODS OF DETERMINATION AND DATA ON THE WATER-SOLUBLE AND TOTAL BORON IN SOME SOILS OF ILLINOIS AND GEORGIA

BY

LAWRENCE CARROLL OLSON

A. B., Augustana College, 1934

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN AGRONOMY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1940.

URBANA, ILLINOIS

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INTRODUCTION

The increased use of boron as a fertilizer and the recognition of a large number of physiological disorders in plants as being due to boron deficiency signify the importance of a study of the boron content of soils and plants. At least, twenty physiological disorders in plants have been definitely associated with boron deficiency and boron has been shown to be a necessary constituent of many plants. There are over 50 boron minerals known but most of these, with the exception of tourmaline, a complex borosilicate of aluminum and other bases, are found in arid and semi-arid regions. Tourmaline is associated with various soil minerals and rocks, such as biotite, muscovite, limestone, hornblende, and slate. Fertilizing materials contain appreciable quantities of boron.

Various soil factors such as parent material, humidity, vegetation and others determine the amount of boron present in a soil, but cropping and fertilization may alter the original boron content to such an extent that it is impossible to make any general statements regarding the boron status of a soil.

Since the methods used for the determination of boron have not been well worked out for soils, a study of the boron in soils necessitates the refinement and improvement of the methods available and the working out of new methods. The purpose of this report is to describe methods for the determination of available and total boron in soils and to report on the boron content of some of the important soil types of Illinois and Georgia.

HISTORICAL

Only a relatively few analyses have been made for boron in soils. The methods of determination fall into two groups: 1) Volumetric and 2) Colorimetric. The volumetric method involves the use of mannite and sodium hydroxide, while quin-

alizarin, turmeric, and other organic compounds have been used in the colorimetric procedures. Table 1 reports the method used and the results obtained by a number of investigators who have made boron analyses on soils from various sections of the United States and surrounding territories as indicated.

The fractions of boron that have been determined are water-soluble, acid-soluble, and total. The analyses made for total boron in soils are very limited.

Table 1. Results of the Analyses of Soils for Water-Soluble, Acid-Soluble and Total Boron as Reported by Various Investigators

Investigator	Location of Samples	Method Used	Reported Results
			ppm. Boron
Wilcox	Western U. S.	Mannite and .023 N.NaOH Water-Soluble	None
Cook and Millar	Michigan	Mannite and .01 N.NaOH Acid-Soluble	.37 to 2.05
Robinson, Whetstone and Byers	Various parts of U. S.	Mannite and .023 N.NaOH Acid-Soluble	1.0 to 45.5
		Total	6.4 to 66.0
Woodbridge	Eastern Canada & British Columbia	Mannite and .02 N.NaOH Acid-Soluble	.05 to 2.32
Scott and Webb	California	Turmeric Paper Water-Soluble	.16 to .93
Naftel	Alabama	Tumeric Extract	None
Berger and Troug	Wisconsin	Quinalizarin Water-Soluble	.50 to .93
		Total	2.0 to 28.3

The methods for water-soluble boron involve the use of boiling water. For acid soluble boron, phosphoric acid, dilute sulfuric acid, and carbonic acid have been used. The total boron determinations reported have involved a fusion with either sodium carbonate or sodium acid phosphate and a separation by either distillation as methyl borate or an extraction with alcohol.

EXPERIMENTAL AND THEORETICAL

When boric acid is titrated with sodium hydroxide it behaves as a very weak monobasic acid and has an indefinite endpoint. The addition of mannite to boric acid forms an indefinite mannitol-boric acid which is more highly ionized than boric acid and thus may be more accurately titrated with sodium hydroxide. Carbon dioxide, phosphoric acid, and buffering substances interfere with the boric acid titration. Studies of this titration method using .01 normal sodium hydroxide, to determine the recovery of boric acid from known solutions ranging from .02 to .30 mg. boron, indicate a recovery of from 90 to 108 per cent. When .02 mg. boron or less is titrated, less than .02 ml. of the base is used, and the percentage error may be quite large. However, the average of triplicate or quadruplicate determinations gives reliable results for this small amount when properly calibrated glass measuring devices are used.

Of the various quinones that have been used for the colorimetric determination of boric acid 1, 2, 5, 8 tetrahydroxyanthraquinone or quinalizarin appears to be most satisfactory. The test is carried out in a medium of sulfuric acid and a color change from violet to blue occurs with increasing amounts of boric acid. Fluorides, nitrates, dichromates, permanganates and other oxidizing substances interfere with the determination. The concentration of the sulfuric acid used in carrying out the quinalizarin determination is rather critical, a concentration of from 92 to 94 per cent by weight sulfuric acid giving the most sensitive reaction. When the concentration of sulfuric acid is kept within this range, .0002 mg. of boron in 1 ml. volume may be detected. Decreasing the concentration of the sulfuric acid makes the test much less sensitive but increases the range over which the test may be applied. When 92 to 94 per cent sulfuric acid is used, amounts of boron above .004 mg. cannot be separated, but when less than 90 per cent sulfuric acid is used, amounts up to .010 mg. of boron can be separated.

A study is made of the adaptability of the quinalizarin method for use in a Cenco-Sheard-Sanford Photelometer. Satis-

factory results are obtained using an orange filter and absorption cells of either 1 cm. or 5 cm. thickness. A spread of 15 to 20 divisions is obtained using the 5 cm. absorption cells and boron concentrations of from 0 to .03 mg. in 10 ml. volume. Single determinations are fairly reproducible but triplicate determinations are much more reliable. One thousandth of a milligram of boron in 10 ml. volume can be quite readily detected.

The effects of time of standing and temperature on the quinalizarin reaction have been studied. Maximum color development is reached at the end of one-half hour and twelve hours standing produces no change in the intensity of the color. A variation in temperature from 65 to 90 degrees Fahrenheit causes a pronounced change in the color of the quinalizarin-boron solutions. At the higher temperatures the color produced by boron becomes less intense.

A comparison of the efficiency of the absorption cells of 1 cm. thickness with the cells of 5 cm. thickness has been studied, and the results appear somewhat more favorable for the thicker cells.

The procedure used for the determination of total boron in soils is fusion with potassium hydroxide followed by either extraction with ethyl alcohol or by extraction with 1:3 sulfuric acid and determination of boron in the extract by the quinalizarin photelometric procedure previously described. Both methods give good results but the sulfuric acid extraction method is more rapid. Triplicate determinations are recommended.

The available boron in soils is determined by extraction with hot water and a subsequent filtration and evaporation of the filtrate after it has been made alkaline. The residue is taken up with 10 normal sulfuric acid and the determination made with the colorimetric method noted above.

RESULTS AND DISCUSSION

The available boron in the Illinois soils studied varies from .20 to 1.22 parts per million. The Georgia soils as a group are much lower in available boron, the range being .01 to .65 parts

per million. The Illinois and Georgia soils contain comparable amounts of total boron, the former group containing 18 to 44 parts per million and the latter 9 to 52.

A limited number of samples of plant material analyzed shows a boron content ranging from 23 to 94 parts per million.

No significant relationship between fertilizer treatment and available or total boron in the soil is apparent. There is no definite relationship between the total boron and the available boron in the soil. However, the total/available boron ratio in the Illinois soils is generally less than 100, while the ratio for Georgia soils ranges from 180 to nearly 400.

SUMMARY

Studies are reported on the titration method using mannite and the quinalizarin colorimetric method for the determination of boron. A method is described involving the use of a photelometer and 90 to 94 per cent sulfuric acid for the determination of total and available boron in soils and plant material. Under certain conditions the quinalizarin test has a sensitivity of .0002 mg. boron. If the concentration of the sulfuric acid falls below 90 per cent by weight, the quinalizarin test is not sufficiently sensitive to determine the small amounts of boron that are found in soils.

Data are presented on the available and total boron in soils of Illinois and Georgia.

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VITA

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The author is a member of Sigma Xi, honorary fraternity in science; Gamma Sigma Delta, honorary fraternity in agriculture; and the American Association for the Advancement of Science.

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